product was isolated from the fast-moving bands. Sublimation of the eluate, 15 mg, yielded XVII: ir (Nujol), C=O, C=C 6.11 μ (s). The ultraviolet spectrum and tlc behavior were identical with those of an authentic sample.[4b,13,14]

trans,trans-**Hexahydrojulolidine (XVId).** **A.** Ketone XVIa, 200 mg, was converted to its semicarbazone in the usual manner. Crystallization from methanol afforded 152 mg of colorless needles of semicarbazone: mp 236–237°; ir (Nujol), NH 2.82 (w), 3.00 (w), 3.18 (m), C=O 5.86 μ (s).

Anal. Calcd for $C_{13}H_{22}ON_4$: C, 62.37; H, 8.89; N, 22.38. Found: C, 61.89; H, 8.83; N, 22.25.

A solution of 500 mg of potassium hydroxide in 5 ml of ethylene glycol was concentrated by distillation to half its volume. The semicarbazone, 160 mg, was added and the solution refluxed for 4 hr. The cooled solution was acidified with 5% hydrochloric acid and all solvents were removed under vacuum. The residue was made basic by the addition of ammonium hydroxide and extracted with chloroform. The extract was dried over anhydrous potassium carbonate and evaporated. The oily residue was converted into a picrate. Crystallization from methanol yielded 78 mg of XVId·picrate, mp, mmp 182° (lit.[16b,d] mp 184°);[17] the infrared spectrum was identical with that of an authentic sample.[17]

B. Sodium borohydride, 200 mg, was added in several portions to a stirring solution of 200 mg of ketone XVIa in 5 ml of methanol. Thereafter the solvent was removed under vacuum and water added to the residue. The aqueous solution was extracted with ether and the extract dried over sodium sulfate and evaporated. Crystallization of the solid residue, 200 mg, from hexane yielded alcohol XVIb, mp 114–116°.

Anal. Calcd for $C_{12}H_{21}ON$: C, 73.79; H, 10.84. Found: C, 74.03; H, 10.76.

A solution of 200 mg of the alcohol and 100 mg of freshly crystallized *p*-toluenesulfonyl chloride in 2 ml of pyridine was left standing at 10° for 12 hr. Chloroform, 20 ml, and excess solid sodium bicarbonate were added and the inorganic salts filtered. The filtrate was washed with ice-water and ice-cold 5% sodium hydroxide solution and dried over potassium carbonate. Solvent removal yielded an oily residue whose last traces of pyridine were removed by distillation of added toluene. Crystallization of the residue from benzene yielded 160 mg of tosylate XVIc: mp 169–171°; ir (Nujol), C=C 6.27 μ (w); pmr, three-proton singlet 2.41 (Me), one-proton multiplets 3.45, 4.12 (aminomethine, tosyloxymethine), AB pair of doublets 7.27 (J = 8.0 cps), 7.75 (J = 8.0 cps) (aromatic H's).

Anal. Calcd for $C_{19}H_{27}O_3NS$: N, 4.01. Found: 3.86.

A suspension of 200 mg of lithium aluminum hydride and 150 mg of the tosylate in 20 ml of tetrahydrofuran was left stirring at room temperature for 12 hr. Sodium sulfate decahydrate was added and the inorganic salts were filtered and washed with ethyl acetate. The combined filtrates were evaporated and the residual oil was transformed into its picrate. Crystallization of the latter from methanol yielded 108 mg of the derivative of XVId, mp, mmp 184°, identical in all respects with an authentic specimen.

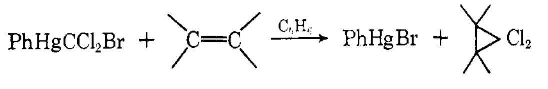
Halomethyl–Metal Compounds. XIX. Further Studies of the Aryl(bromodichloromethyl)mercury–Olefin Reaction[1]

Dietmar Seyferth, Jeffrey Yick-Pui Mui,[2] and Robert Damrauer[3]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received April 20, 1968*

Abstract: Kinetic studies of the reactions of substituted aryl(bromodichloromethyl)mercury compounds, p-$ZC_6H_4HgCCl_2Br$ (Z = H, Cl, F, Me, MeO), with $Me_2C{=}CMeEt$ in benzene solution at 39.0° showed that the rate of CCl_2 extrusion from these mercurials differs only slightly as a function of Z. This insensitivity to electronic factors is taken as evidence in support of a concerted CCl_2 extrusion process proceeding *via* the cyclic transition state I. A study of reactions in which two different substituted styrenes were allowed to compete for a deficiency of phenyl(bromodichloromethyl)mercury-derived dichlorocarbene gave the following relative rate constants: p-$CH_3C_6H_4CH{=}CH_2$, 1.52; $C_6H_5CH{=}CH_2$, 1.00; p-$FC_6H_4CH{=}CH_2$, 0.961; p-$ClC_6H_4CH{=}CH_2$, 0.839; m-$CF_3C_6H_4$-$CH{=}CH_2$, 0.453. These data correlate well with the Hammett equation and give ρ -0.619 ± 0.045 using σ^+ constants. The addition of CCl_2 to the olefinic C=C bond thus appears to be a concerted, electrophilic addition in which the transition state is but slightly polar, as shown in II.

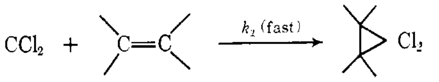
A recent kinetic study of the reaction of phenyl(bromodichloromethyl)mercury with olefins, which gives *gem*-dichlorocyclopropanes in high yield[4] (eq 1), showed that a free carbene mechanism as indicated



(1)

in eq 2 and 3 was operative.[5] However, a more detailed understanding of the individual steps of this reaction sequence seemed desirable. This report concerns further studies of the mercurial decomposition step

$$PhHgCCl_2Br \underset{k_{-1}\,(\text{fast})}{\overset{k_1\,(\text{slow})}{\rightleftharpoons}} PhHgBr + CCl_2 \qquad (2)$$



(3)

(*i.e.*, the factors which influence k_1) and the CCl_2 + olefin reaction step (k_2).

The Mercurial Decomposition Step. In our previous study it was found that the rate of *gem*-dichlorocyclopropane formation in the $PhHgCCl_2Br$–$Me_2C{=}CMeEt$ reaction was independent of the initial olefin concentration and first order in mercurial concentration.[5] In the case of this olefin, which was the most reactive (in such reactions) of a series examined in competition studies,[6] it appears that k_2 is much larger than k_{-1}, so that the rate expression (eq 4) for the eq 2–3 reaction

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[1] Part XVIII: D. Seyferth, M. E. Gordon, and K. V. Darragh, *J. Organometal. Chem.*, in press.

[2] Postdoctoral Research Associate, 1966–1967.

[3] National Institutes of Health Predoctoral Fellow, 1964–1967.

[4] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, 87, 4259 (1965).

[5] D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *ibid.*, 89, 4953 (1967).

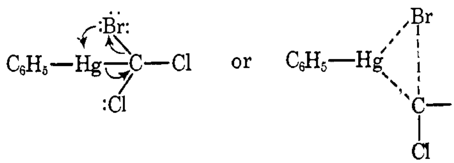
[6] D. Seyferth and J. M. Burlitch, *ibid.*, 86, 2730 (1964).

sequence simplifies to eq 5. In other words, in the

$$\frac{dx}{dt} = \frac{k_1[\mathrm{PhHgCCl_2Br}]}{1 + (k_{-1}[\mathrm{PhHgBr}]/k_2[\mathrm{olefin}])} \qquad (4)$$

$$\frac{dx}{dt} = k_1[\mathrm{PhHgCCl_2Br}] \qquad (5)$$

case of this very reactive olefin, the measured rate is the actual rate of the mercurial decomposition essentially uncomplicated by the reverse reaction between phenylmercuric bromide and dichlorocarbene. The rates of the $PhHgCCl_2Br$-$Me_2C{=}CMeEt$ reaction measured at 39.0, 49.9, and 60.4° provided data which allowed the calculation of $\Delta S^{\ddagger} = -2.8$ eu and a frequency factor Z ($p = 1$) of 0.4×10^{13}. The numerically small $\Delta S^{\ddagger}$ spoke against ionic character in the mercurial decomposition transition state and the values of $\Delta S^{\ddagger}$ and Z were in agreement with what would be expected for a unimolecular, concerted process. Accordingly, we suggested transition state I for the CCl_2 extrusion process.



I

It was hoped that a study of the effects of appropriate substituents in the *para* position of aryl(bromodichloromethyl)mercury compounds, p-$ZC_6H_4HgCCl_2Br$, on the rate of their decomposition in the presence of the efficient CCl_2 scavenger $Me_2C{=}CMeEt$ would provide further information concerning the nature of this CCl_2 extrusion process. The p-$ZC_6H_4HgCCl_2Br$ compounds, where Z is Cl, F, CH_3, and OCH_3, were prepared by the usual mercurial synthesis procedure,[7] and their rates of reaction with $Me_2C{=}CMeEt$ to give 1,1-dichloro-2-ethyl-2,3,3-trimethylcyclopropane were measured using the general procedures of our previous study.[5] Table I summarizes the observed rates of reaction and the rate constants, k_1, derived on the assumption that the rate equation (eq 5) is applicable.

Table I. Reactions of p-$ZC_6H_4HgCl_2Br$ (0.099 *M*) and $Me_2C{=}CMeEt$ (0.20 *M*) in Benzene at 39.0°

Z	dx/dt, mol/l. min × 10^5	k_1, min^{-1} × 10^4
H	8.8	8.9
Cl	8.0	8.1
F	7.5	7.6
CH_3	7.1	7.2
OCH_3	6.6	6.7

The data in Table I show that there is no pronounced *para* substituent dependence of the rate of dichlorocarbene extrusion from the p-$ZC_6H_4HgCCl_2Br$ reagents. We note that k_1 increases very slightly as the electron-donating properties of Z decrease (excluding the Z = H mercurial), but we hesitate to discuss such small differences, especially since we estimate that the uncertainty in the dx/dt determinations for the mercurials where Z = Cl, F, Me, and OMe is ±10%, rather than the ±5% in the case of $C_6H_5HgCCl_2Br$ itself. In any case, this decomposition of $ArHgCCl_2Br$ compounds, which involves Hg–C bond cleavage, differs markedly from other reactions in which arylmercury bonds are broken in terms of the electronic effects which have been observed. Some examples of such reactions are given in Scheme I. All of these reactions clearly involve electrophilic attack at the *C*–Hg bond (S_E2 reactions). Although we are aware of no similar quantitative studies of nucleophilic substitution at mercury (*e.g.*, $ZC_6H_4HgCl + I^- \rightarrow$), we would anticipate to find that correlation of σ constants with log k_2 would give large, positive values of ρ. We therefore suggest that the small differences between the rate constants listed in Table I can best be rationalized in terms of the cyclic transition state (I) suggested in our previous paper.[5] The electronic effects of Z, if apparent at all, thus are virtually balanced out in the concerted Hg–Br bond making and Hg–C bond breaking. We have assumed in this discussion that eq 5 is applicable. We do not know how the rates of the ZC_6H_4HgBr–CCl_2 reactions differ as Z is varied, but, in any case, the reverse reaction (k_{-1}) is not important in our present experiments in which an initial olefin concentration of 0.20 *M* and an initial mercurial concentration of ~0.1 *M* were used, and in which only a small extent of reaction was measured. This ensures that the denominator in eq 4 ≅ 1, *i.e.*, that eq 4 reduces to eq 5.

Scheme I

$$(p\text{-}ZC_6H_4)_2Hg + HCl \xrightarrow{\text{DMSO-dioxane, 32°}} p\text{-}ZC_6H_4HgCl + p\text{-}ZC_6H_5$$

[$(\sigma + \sigma^+)/2$ *vs.* log k gives $\rho = -2.8$[8]]

$$(p\text{-}ZC_6H_4)_2Hg + HgI_2 \xrightarrow{\text{dioxane, 25°}} 2p\text{-}ZC_6H_4HgI$$

[σ *vs.* log k_2 gives $\rho = -5.87$[9]]

$$(p\text{-}ZC_6H_4C{\equiv}C)_2Hg + HCl \xrightarrow{\text{DMSO-dioxane, 32°}} p\text{-}ZC_6H_4C{\equiv}CHgCl + p\text{-}ZC_6H_4C{\equiv}CH$$

[$(\sigma + \sigma^+)/2$ *vs.* log k gives $\rho = -1.0$[10]]

$$ZC_6H_4HgCl + HCl \xrightarrow{\text{EtOH-H}_2\text{O, 70°}} ZC_6H_5 + HgCl_2$$

[σ^+ *vs.* log k gives $\rho = -2.44$[11]]

$$ZC_6H_4HgBr + I_2 \xrightarrow{\text{pyridine}} ZC_6H_4I + IHgBr$$

[σ *vs.* log k_2 gives $\rho = -2.87$[12]]

A transition state such as I, in which intramolecular nucleophilic attack by a halogen substituent on the methyl carbon atom at mercury is involved, provides ready explanation for the observed fact that $PhHgCBr_3$, $PhHgCClBr_2$, and $PhHgCCl_2Br$ are so much more reactive in cyclopropanation reactions than is $PhHgCCl_3$.[4] The fact that $PhHgCCl_2Br$ gives exclusively PhHgBr and CCl_2 also can be understood in terms of transition state I, both steric and electronic factors tending to favor the developing Br–Hg overlap over the alternative Cl–Hg overlap.

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[7] D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, **4**, 127 (1965).

[8] R. E. Dessy and J.-Y. Kim, *J. Amer. Chem. Soc.*, **82**, 686 (1960).

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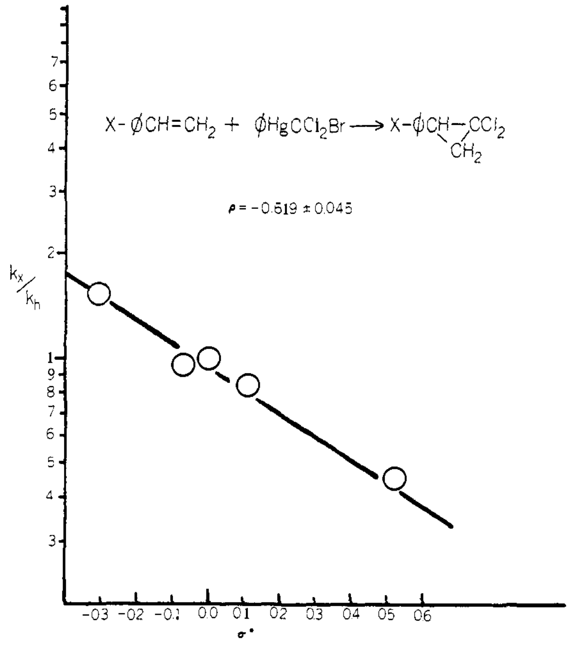

Figure 1. Plot of log k_{rel} *vs.* σ^+ values for the reaction of phenyl(bromodichloromethyl)mercury-derived dichlorocarbene with substituted styrenes.

The Dichlorocarbene–Olefin Reaction. In a previous study[6] relative reactivities of various alkyl-substituted olefins toward $PhHgCCl_2Br$-derived dichlorocarbene were measured. The observed k_{rel} values for the olefin–$PhHgCCl_2Br$ reaction at 80° (*vs.* cyclohexene = 1) were identical within experimental error to k_{rel} values determined for the reaction of sodium trichloroacetate derived dichlorocarbene with the same olefins, also at 80°. The order of decreasing olefin reactivity was $Me_2C{=}CMeEt$, 22.5; $Et_2C{=}CHMe$, 3.55; Et(*n*-Pr)$C{=}CH_2$, 2.07; cyclohexene, 1.0; *cis*-*n*-$PrCH{=}CHEt$, 0.83; *trans*-*n*-$PrCH{=}CHEt$, 0.52; *n*-C_5H_{11}-$CH{=}CH_2$, 0.24. These results indicated that electronic effects predominated over steric effects in determining olefin relative reactivities toward CCl_2. However, later studies provided evidence which showed that steric effects in the addition of $PhHgCCl_2Br$-derived dichlorocarbene to olefins are not negligible,[13,14] and thus it seemed desirable to determine the relative reactivities of olefins toward mercurial-derived dichlorocarbene in which the steric factor in the olefin remained constant throughout the series, so that electronic effects alone could be assessed. Accordingly, we have carried out a Hammett study of the reaction of a series of substituted styrenes with phenyl(bromodichloromethyl)mercury in benzene solution at 80.3 ± 0.1°.

In these experiments phenyl(bromodichloromethyl)mercury and a five- to tenfold excess of two styrenes in benzene solution were stirred under nitrogen at the specified temperature for 2 hr. Direct gas–liquid partition chromatographic (glpc) analysis of the reaction mixtures served to determine the yields of the two 1-aryl-2,2-dichlorocyclopropanes produced, and from these and the starting concentrations of the styrenes the relative reactivities of the styrenes used could be calculated by the equation[15]

$$k_{\text{rel}} = k_a/k_b = P_a I_b / I_a P_b$$

where P_a and P_b are the moles of product derived from olefin "a" and "b," respectively, and I_a and I_b are the initial moles of olefins "a" and "b" present at the beginning of the reaction. (The validity of this equation for the relative rate constant depends upon the starting olefins, "a" and "b," being present in large excess, so that their effective concentration does not change significantly during the course of the reaction.) Duplicate experiments could be carried out with high precision. Control experiments established that the substituted styrenes used as well as the 1-aryl-2,2-dichlorocyclopropanes produced were stable to the reaction conditions and to analysis by glpc. The results of this study are presented in Table II.

Table II. Relative Rate Constants of the Addition of $PhHgCCl_2Br$-Derived Dichlorocarbene to Substituted Styrenes, $XC_6H_4CH{=}CH_2$

X in $XC_6H_4CH{=}CH_2$	k_X/k_H (av)
p-CH_3	1.52
H	1.00
p-F	0.961
p-Cl	0.839
m-CF_3	0.453

Inspection of the results in Table II indicates immediately that electrophilic attack at the C=C bond is occurring. The relative rate constant data correlate very well with the Hammet equation; the ρ value using σ^+ constants[16] was computed to be −0.619 ± 0.045 (*cf.* Figure 1). Poorer correlations were obtained when σ or σ^0 constants were used. Brown's σ^+ constants differ from ordinary σ constants in that strong resonance interactions of *para* substituents with the electron-deficient carbon adjacent to the aryl group are taken into account; they have been particularly useful in correlating data in electrophilic substitution reactions.[16] The value obtained, −0.619 ± 0.045, is virtually identical with the value of ρ obtained in a study of the insertion of phenyl(bromodichloromethyl)mercury-derived dichlorocarbene into the Si–H bonds of substituted aryldimethylsilanes (−0.632 ± 0.031).[1] The conclusion to be drawn from the present Hammett study, therefore, is essentially the same—that the transition state of the addition of dichlorocarbene to the olefinic double bond of substituted styrenes (*i.e.*, more generally, of reaction 3) is a slightly polar one. The dichlorocarbene is an electrophilic reagent, and one may safely conclude that the dichlorocyclopropanation of olefins is essentially a concerted electrophilic addition, II. Singlet-state divalent carbon species (*e.g.*, CCl_2) are isoelectronic with trigonal boron compounds, and thus it is not surprising that the rates of hydroboration of substituted styrenes also showed relatively little dependence on the nature of the substituent. A relatively nonpolar, π-complex-like

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[13] D. Seyferth, M. E. Gordon, J. Y.-P. Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, **89**, 959 (1967).

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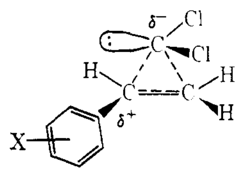
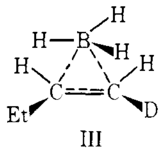


II

transition state was discussed by these investigators,[17a] and it may be noted in this connection that a three-center, π-complex transition state (III) for hydrobora-



III

tion seems to be favored on the basis of other results.[17b] The similarity between the olefin cyclopropanation transition state suggested by us (II) and that proposed for olefin hydroboration is striking. The formation of silver ion π complexes of substituted styrenes also was found to have a numerically small, negative ρ value (−0.766),[18] but addition reactions to the C=C bonds of substituted styrenes which involve intermediates with fully developed charge are characterized by high ρ values (hydration, $\rho = -4$[19]; bromination in methanol solutions, $\rho = -4.3$[20]).

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen. Elemental analyses were performed by Dr. S. M. Nagy (MIT Microchemical Laboratory) and by the Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded using either a Perkin-Elmer 237 or 337 grating infrared spectrophotometer. The proton magnetic resonance spectra were recorded in solution with a Varian Associates A-60 nmr spectrometer.

Preparation of Substituted Aryl(bromodichloromethyl)mercury Compounds. Diarylmercury compounds, $(p\text{-}ZC_6H_4)_2Hg$, were available from another study in these laboratories[21] and were converted in essentially quantitative yields to the corresponding arylmercuric halides by reaction with an equimolar quantity of mercuric chloride in THF–benzene. The $ZC_6H_4HgCCl_2Br$ compounds, where Z = H, Cl, Me, and MeO, were prepared by the standard procedure as described in detail earlier—the reaction of the arylmercuric chloride, bromodichloromethane, and potassium *t*-butoxide in benzene.[7] Yield and physical and analytical data are given as follows: ***p*-chlorophenyl(bromodichloromethyl)mercury**, 50% yield, mp 129–130° dec (*Anal.* Calcd for $C_7H_4BrCl_3Hg$: C, 17.70; H, 0.85. Found: C, 17.57; H, 0.86; ***p*-toly(bromodichloromethyl)mercury**, 75% yield, mp 116–117° dec (*Anal.* Calcd for $C_8H_7BrCl_2Hg$: C, 21.14; H, 1.55. Found: C, 21.36; H, 1.75); nmr spectrum ($CDCl_3$), singlet at 1.73 ppm (3 H) and singlet at 7.16 ppm downfield from internal tetramethylsilane (4 H); ***p*-anisyl(bromodichloromethyl)mercury**, 77% yield, mp 104–105° dec (turned brick-red) (*Anal.* Calcd for $C_8H_7BrCl_2OHg$: C, 20.41; H, 1.50. Found: C, 20.33; H, 1.56), nmr spectrum ($CDCl_3$), singlet at 3.79 ppm (3 H) and a complex multiplet at 7.08 ppm (4 H).

***p*-Fluorophenyl(bromodichloromethyl)mercury** was prepared in a variation of the original procedure in which benzene is replaced by diethyl ether as solvent, a modification first reported by Finnish workers.[22] Into a 500-ml Morton flask *equipped with a high-speed stirrer*, a nitrogen inlet tube, and a large-diameter rubber connecting tube leading to a flask containing 97 mmol of previously prepared, solid potassium *t*-butoxide was charged 48.5 mmol of *p*-fluorophenylmercuric chloride, 0.19 mol of bromodichloromethane, and 220 ml of freshly dried and distilled diethyl ether under an atmosphere of dry nitrogen. The contents were cooled to −20° with a Dry Ice–acetone bath and subsequently the potassium *t*-butoxide was added *with vigorous stirring* in small portions over a period of 20 min. A creamy suspension resulted. The reaction mixture was then allowed to warm to room temperature and was hydrolyzed with *ca.* 150 ml of distilled water. The ether layer was separated, washed with two 150-ml portions of water, dried over anhydrous magnesium sulfate, and evaporated to dryness at reduced pressure. The product (20.0 g, 90% crude yield, mp 110° dec) was recrystallized twice from chloroform-*n*-hexane. A total of 16.95 g (77%) of pure $p\text{-}FC_6H_4HgCCl_2Br$, mp 113° dec, was isolated. *Anal.* Calcd for $C_7H_4BrCl_2FHg$: C, 18.33; H, 0.87; F, 4.14; Cl, Br, 32.88. Found: C, 18.09; H, 0.78; F, 4.42; Cl, Br, 32.37. This procedure also serves excellently in the preparation of phenyl(bromodichloromethyl)mercury.

All of the mercurials prepared were examined by means of thin layer chromatography.[7] In all cases only a trace amount of impurity could be detected. The purified mercurials were stored at −5° (no longer than 3 days) prior to use. *p*-Anisyl(bromodichloromethyl)mercury had to be used immediately after it had been prepared, since it turned light pink within 24 hr at −5° and brick-red after several days.

The $p\text{-}ZC_6H_4HgCCl_2Br$ + $Me_2C{=}CMeEt$ Reaction. Kinetic Runs. The procedure used was identical with that of our previous kinetic study of $PhHgCCl_2Br$ + olefin reactions, and the reader is refered to the Experimental Section of our previous paper.[5] In the present study, the progress of the reactions was followed by glpc determination of the 1,1-dichloro-2-ethyl-2,3,3-trimethylcyclopropane formed. *o*-Dichlorobenzene was used as internal standard. The experimental data are given in Table III. A plot of the concentration of 1,1-dichloro-2-ethyl-2,3,3-trimethylcyclopropane *vs.* time in minutes gave in each case a straight line, the slope of which was the rate of the reaction, d*x*/d*t*. The results are given in Table III.

Table III. The $p\text{-}ZC_6H_4HgCCl_2Br$ + $Me_2C{=}CMeEt$ Reaction. Kinetic Data[a]

	Z in $p\text{-}ZC_6H_4HgCCl_2Br$				
	MeO	Me	H	F	Cl
Time, min	Concn of 1,1-dichloro-2-ethyl-2,3,3-trimethylcyclopropane, $M \times 10^2$				
5	0.035	0.032	0.050	0.035	0.040
10	0.057	0.070	0.083	0.060	0.075
15	0.101	0.117	0.131	0.110	0.125
20	0.126	0.139	0.176	0.148	0.159
25	0.161	0.176	0.250	0.189	0.196
30	0.191	0.213	0.273	0.225	0.232
35	0.224	0.249	0.315	0.266	0.280
40	0.266	0.288	0.362	0.303	0.326
45	0.292	0.309	0.395	0.332	0.360
50	0.337	0.354	0.446	0.379	0.404
55	0.369	0.386	0.504	0.416	0.428
60	0.398	0.430	0.532	0.448	0.458
	d*x*/d*t*, mol/l. min × 10^5				
	6.6	7.1	8.8	7.5	8.0
	k_1, min^{-1} × 10^4				
	6.7	7.2	8.9	7.6	8.1

[a] Initial concentrations: mercurial, 0.099 *M*; olefin, 0.20 *M*. Reactions in benzene solution at 39.0°.

Preparation and Characterization of 1-Aryl-2,2-dichlorocyclopropanes. Two reactions were run in each case—one on a 20-mmol scale using an 1:1 ratio of $PhHgCCl_2Br$ and substituted styrene in order to obtain samples of product for characterization and determination of response factors and one in which a reaction of *ca.* 1 mmol of the styrene with *ca.* 4 mmol of the mercurial was run for yield determination. In all cases the reactions were carried out

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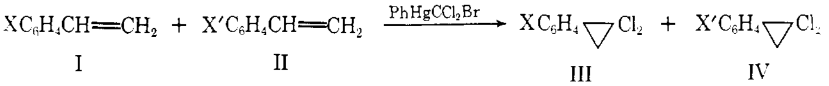
Table IV. Competition Experiments between Substituted Styrenes for Phenyl(bromodichloromethyl)mercury



X	X′	I, g	I, mmol	II, g	II, mmol	C_6H_5Hg-CCl_2Br, g	C_6H_5Hg-CCl_2Br, mmol	Yield of III, %	III, mmol	Yield of IV, %	IV, mmol	$k_X/k_{X'}$	Av k_X/k_H
p-CH_3	H	0.4154	3.52	0.3954	3.80	0.2402	0.545	58.7	0.320	41.5	0.226	1.53	1.52
p-CH_3	H	0.4201	3.56	0.4045	3.88	0.2159	0.490	56.8	0.278	40.6	0.199	1.52	
p-F	*p*-Cl	0.4634	3.79	0.4986	3.60	0.2345	0.532	55.7	0.296	43.6	0.252	1.12	0.961
p-F	*p*-Cl	0.4806	3.93	0.5150	3.72	0.2277	0.517	53.3	0.275	42.9	0.222	1.17	
m-CF_3	*p*-Cl	0.5925	3.44	0.5106	3.68	0.2008	0.456	32.3	0.147	64.0	0.292	0.538	0.453
m-CF_3	*p*-Cl	0.5916	3.44	0.5310	3.83	0.2079	0.472	32.0	0.151	65.8	0.310	0.542	
p-Cl	H	0.5010	3.61	0.3971	3.81	0.2194	0.498	45.7	0.228	57.4	0.286	0.842	0.839
p-Cl	H	0.4449	3.21	0.4002	3.84	0.2227	0.505	40.7	0.206	58.5	0.295	0.836	

under nitrogen in benzene solution at 80.3°. The general work-up procedure for mercurial–olefin reactions[4] was used. In the first set of experiments product samples were isolated by distillation; in the second set, yield determination was accomplished by glpc, using an F & M Model 700 gas chromatograph with a commercial 6 ft × 0.25 in. 20% UCW98 silicone rubber on Chromosorb W column (40–200° temperature program). The products are given as follows: **1,1-dichloro-2-phenylcyclopropane**, 93% yield, bp 38–39° (0.07 mm), n^{20}D 1.5519 (lit.[23] n^{23}D 1.5501) (*Anal.* Calcd for $C_9H_8Cl_2$: C, 57.78; H, 4.31; Cl, 37.91. Found: C, 57.63; H, 4.27; Cl, 37.90); **1,1-dichloro-2-*p*-tolylcyclopropane**, 82% yield, bp 54–55° (0.12 mm), n^{20}D 1.5472 (lit.[24] n^{20}D 1.5460) (*Anal.* Calcd for $C_{10}H_{10}Cl_2$: C, 59.73; H, 5.01; Cl, 35.26. Found: C, 59.19; H, 5.16; Cl, 35.45); **1,1-dichloro-2-*p*-fluorophenylcyclopropane**, 92% yield, bp 44–45° (0.12 mm), n^{20}D 1.5303 (*Anal.* Calcd for $C_9H_7Cl_2F$: C, 52.71; H, 3.44; Cl, 34.58. Found: C, 52.74; H, 3.64; Cl, 34.41); **1,1-dichloro-2-*p*-chlorophenylcyclopropane**, 84% yield, bp 64–65° (0.1 mm), n^{20}D 1.5673 (lit.[25] n^{20}D 1.5672); **1,1-dichloro-2-*m*-trifluoromethylphenylcyclopropane**, 90% yield, bp 49–50° (0.14 mm), n^{20}D 1.4902 (*Anal.* Calcd for $C_{10}H_7Cl_2F_3$: C, 47.09; H, 2.77; Cl, 27.80. Found: C, 47.34; H, 2.73; Cl, 27.27).

1,1-Dichloro-2-*p*-anisylcyclopropane was obtained in only very low yield, and for this reason the *p*-methoxystyrene–mercurial reaction was not included in the competition study. In the 20-mmol scale reaction filtration of phenylmercuric bromide (84%) and removal of solvent left 2.0 g of a blue liquid, the distillation of which at 0.06 mm gave only 0.08 g of pure product, bp 72–73° (0.06 mm), n^{20}D 1.5565 (lit.[25] n^{20}D 1.5564).

Infrared, nmr, and mass spectra were obtained for all of these 1,1-dichloro-2-arylcyclopropanes and served to confirm the structures given. Tabulations of the spectra are available in the Ph.D. thesis of R. D. (Massachusetts Institute of Technology, Cambridge, Mass., 1967).

General Comments Concerning the Competition Experiments. The apparatus used was washed with 5% sulfuric acid, rinsed with water and then with acetone, and dried at 140°. The competition runs were carried out in duplicate (two at a time) in a Sargent viscosimeter bath. The temperature was regulated to 80.3 ± 0.1°. The reactions were carried out under nitrogen with magnetic stirring for 2 hr. Each of the substituted styrenes used was distilled under vacuum until its purity (*via* glpc) was at least 99%. The yields of the 1,1-dichloro-2-arylcyclopropanes produced were determined by glpc using the conditions described above. The internal standard (chlorobenzene or *n*-octane) method was used in yield calculation. The relative rate constants were calculated using the equation of Doering and Henderson.[15]

The relative rate constants thus obtained were analyzed using an IBM 1620 computer, the data being fit to the best straight line for σ, σ^0, and σ^+ constants using a least-squares program. The following values of ρ were obtained: using σ constants, -0.764 ± 0.092; using σ^0 constants, -0.756 ± 0.138; using σ^+ constants, -0.619 ± 0.045.

The general procedure used is illustrated by the competition of styrene and *p*-methylstyrene for phenyl(bromodichloromethyl)mercury. Into a dry, nitrogen-purged, 50-ml three-necked flask equipped with a magnetic stirring unit and a reflux condenser with a nitrogen inlet system was charged 0.3954 g (3.80 mmol) of styrene, 0.4154 g (3.52 mmol) of *p*-methylstyrene, 0.2402 g (0.545 mmol) of $PhHgCCl_2Br$, and 5.0 ml of dry benzene. The mixture was stirred and heated at 80.3 ± 0.1° for 2 hr. Direct glpc analysis (chlorobenzene internal standard) showed that 1,1-dichloro-2-phenylcyclopropane was present in 41.5% yield, 1,1-dichloro-2-*p*-tolylcyclopropane in 58.7% yield Experimental data for these competition experiments are given in Table IV.

Control Experiments. Samples of the 1,1-dichloro-2-arylcyclopropanes produced in these reactions were heated in benzene in the presence of phenylmercuric bromide. In all cases the recovery of the cyclopropanes (*via* glpc) was quantitative.

A further check on the methods used was made by determining both the 1,1-dichloro-2-arylcyclopropanes produced and the substituted styrenes recovered. A mixture of 1.90 mmol of styrene, 1.64 mmol of *p*-methylstyrene, and 0.489 mmol of phenyl(bromodichloromethyl)mercury in 5.0 ml of benzene was heated as before at 80.3° for 2 hr. Direct glpc analysis showed the following components to be present in the reaction mixture: styrene, 1.71 mmol; *p*-methylstyrene, 1.38 mmol; 1,1-dichloro-2-phenylcyclopropane, 0.208 mmol; 1,1-dichloro-2-*p*-tolylcyclopropane, 0.287 mmol. Thus 1.92 mmol (*vs.* 1.90) of the starting styrene is accounted for and 1.67 (*vs.* 1.64) mmol of the starting *p*-methylstyrene. The sum of the cyclopropanes, 0.495 mmol, agrees very well with the amount of mercurial used, 0.489 mmol.

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